

35a

1 564 259

PATENT SPECIFICATION

(11) 1 564 259

- (21) Application No. 46623/77 (22) Filed 9 Nov. 1977
(31) Convention Application No. 2651505
(32) Filed 11 Nov. 1976 in
(33) Federal Republic of Germany (DE)
(44) Complete Specification published 2 April 1980
(51) INT CL³ C08G 18/83/C08L 75/04
(52) Index at acceptance



C3R 32D11A 32D12 32D15 32D16A 32D16B 32D16C 32D16D
32D1 32D6C 32D6H 32D6J 32D6K 32D6L 32D7 32D8
32D9B1 32D9C 32D9F 32E10 32E12 32E1 32E2A
32E2DX 32E2E 32E2Y 32E3A 32E3D 32E3E 32E3Y
32E4 32E6 32E7C 32E7Y 32E8 32E9 32F2 32F3 32F4
32F5 32G2A 32G2C 32G2Y 32H5B2 32H5BY 32H8
32J1A 32J1X 32J1Y 32J2C 32J2D 32J2F 32J2Y 32J3A
32J3X 32J3Y 32J9D 32J9X 32KC 32KE 32KH 32KJ 32S
32T2B 32T2C 32T2X C14A C16 C22 C27 C2A C33A
C5B1 C6A1 C6B C6X C8P L1B L2A L2X L4B L5A
L5C L6A L6G L6H

(72) Inventors PETER MARKUSCH
KLAUS NOLL and
DIETER DIETERICH

(54) ELECTROLYTE-STABLE, WATER-DISPERSIBLE, CATIONIC POLYURETHANE ELASTOMERS

(71) We, BAYER AKTIENGESellschaft, a body corporate organised under the laws of Germany, of 509 Leverkusen, Germany; do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Aqueous dispersions of polyurethanes or polyurethane ureas have long been known (cf. for example, Angewandte Chemie, 82, (1970) pages 53 to 63; DT-OS Nos. 2,314,512 and 2,314,513) and have a high quality level.

Not least the fact that many of these dispersions are free from emulsifiers contributes towards this high quality level. They contain chemically incorporated hydrophilic centres which make the otherwise hydrophobic elastomers self-emulsifying.

The hydrophilic centres incorporated in known water-dispersible polyurethanes and polyurethane ureas may be both salt-like, i.e. ionic groups, and also hydrophilic non-ionic groups.

The first of these two types of polyurethanes known as "polyurethane ionomers", include both polyurethanes containing chemically fixed cations, i.e., in particular, chemically incorporated ammonium ions, and also polyurethanes containing chemically fixed anions, i.e. in particular, incorporated sulphate or carboxylate groups. The second of these two types of polyurethanes, i.e. non-ionic water-dispersible polyurethanes, include, in particular, the polyurethanes and polyurethane ureas containing lateral polyethylene oxide chains according to DT-OS Nos. 2,314,512 and 2,314,513.

The dispersions of these polyurethanes have different characteristic property spectrums, depending upon the type of hydrophilic centre. Thus, polyurethane ionomer dispersions are stable against heating to boiling point because the solubility of the salt groups present in them is substantially unaffected by temperature, whereas non-ionic dispersions coagulate when heated to only a moderate temperature (about 60°C) because the polyethylene oxide side-chains gradually lose their solubility in water at elevated temperature. Unlike ionomers, however, these dispersions are unaffected by the addition of substantially unlimited quantities of electrolytes and are even stable after freezing and thawing.

The sensitivity to electrolytes of cationic polyurethanes is particularly high. Polyurethanes containing quaternary ammonium or tertiary sulphonium groups dispersed in water coagulate immediately, even when only very small quantities of

an electrolyte containing monofunctional ions, such as sodium chloride, in aqueous solution are added to them. On account of this property, considerable problems are involved in the production and use of cationic polyurethane dispersions. Thus, the water which is substantially free from ions generally has to be used for the production thereof. "Hard" water undesirably coarsens the dispersed particles or leads to partial coagulation.

In many cases, cationic dispersions are difficult to pigment because ions adsorbed on the surface of the pigment make the pigment difficult to incorporate and give rise to inhomogeneities. The extraordinary sensitivity of cationic polyurethane dispersions to various types of additives has made them very difficult or even impossible to use on a commercial scale. On the other hand, cationic dispersions have particularly desirable properties, for example extremely good adhesion to various substrates and an excellent film-forming capacity, even in cases where the coatings are extremely hard.

The present invention provides a new water-dispersible cationic polyurethanes which, in the form of an aqueous dispersion, combine the advantage of excellent resistance to frost and electrolytes with the advantage of very high temperature stability. It has surprisingly been found that water-dispersible cationic polyurethane elastomers of this type may be produced when both lateral or terminal hydrophilic chains containing ethylene oxide units and also cationic terminal groups are incorporated into the polyurethane.

This is entirely surprising because it was found that mixtures of aqueous dispersions of ionic and non-ionic polyurethanes definitely do not have this combination of desirable properties. On the contrary, mixtures such as these above all have the disadvantage of the individual constituents.

By incorporating hydrophilic polyether segments either at the ends of the main polymer chain or in the form of side-chains, the cationic polyurethanes are protected surprisingly effectively against the effect of electrolytes. The dispersions are no longer precipitated by dilute sodium chloride solution.

The dispersions according to the present invention are distinguished from products in which the hydrophilic polyether segments are distributed statistically over the entire main polymer chain by their particularly favourable rheological behaviour. The dispersed particles show only moderate swelling which is largely confined to the peripheral zone, so that a favourable relationship between the solids content of the dispersion and its viscosity is obtained. 40%, by weight, dispersions are still free flowing.

Accordingly, the present invention relates to electrolyte-stable, water-dispersible elastomeric polyurethane cationomers, characterised by:

- (a) one or more lateral or terminal polyalkylene oxide-polyether chains containing from 2 to 10%, by weight, of ethylene oxide units, based on the total polyurethane;
- (b) a content of



and/or

groups of from 16 to 100 milliequivalents per 100 g of polyurethane. The invention also relates to aqueous dispersions of the polyurethane cationomers as defined above. Preferably, the dispersion is also characterised by:

- (c) an average particle size of the dispersed polyurethane of <300 mμ; and
- (d) a solids content of from 10 to 45%, by weight.

Furthermore, the present invention also relates to a preferred process for producing the water-dispersible polyurethane elastomer according to the present invention having a substantially linear molecular structure by reacting an organic diisocyanate with an organic compound which is difunctional in the isocyanate-polyaddition reaction containing terminal isocyanate-reactive hydrogen atoms and having a molecular weight of from 300 to 6000, in the presence of synthesis components (a) and (b) containing hydrophilic groups or groups convertible thereto which guarantee the dispersibility of the polyurethane, the at least partial conversion of the latter groups into hydrophilic groups taking place during or after

3

§

10

15

20

25



30

40

9

55

60

(2) the poly(lactones known in polyurethane chemistry, such as the polymers of ϵ -caprolactone started with the above-mentioned dihydric alcohols;

(3) the polycarbonates known in polyurethane chemistry which may be obtained, for example, by reacting the above-mentioned diols with diaryl carbonates or with phosgene;

(4) the polyethers known in polyurethane chemistry, such as the polymers and copolymers of styrene oxide, propylene oxide, tetrahydrofuran, butylene oxide or epichlorohydrin obtained using dihydric starter molecules, such as water, the above-mentioned diols or amines containing 2 NH-bonds. Ethylene oxide may also be used with the proviso that the polyether used contains at most 10% by weight, of ethylene oxide. In general, however, polyethers obtained without ethylene oxide are used;

(5) the polythioethers, polythio mixed ethers and polythioether esters known in polyurethane chemistry;

(6) the polyacetals, for example of the above-mentioned diols and formaldehyde, known in polyurethane chemistry; and also

(7) difunctional terminal polyether esters containing isocyanate-reactive groups.

Dihydroxy polyesters, dihydroxy polylactones, dihydroxy polyethers and dihydroxy polycarbonates are preferably used in the process according to the present invention.

Basically, however, the compounds according to the present invention may also be produced without relatively high molecular weight polyhydroxyl compounds, i.e. using only diisocyanates and low molecular reactants (molecular weight <300).

Chain-extenders having a molecular weight of below 300 which may also be used in the process according to the present invention for producing the self-dispersible polyurethanes are, for example, the low molecular weight diols described above with reference to the production of the dihydroxy polyesters or diamines, such as diaminoethane, 1,6-diaminohexane, piperazine, 2,5-dimethyl piperazine, 1-amino-3-aminomethyl-3,5,5-trimethyl cyclohexane, 4,4'-diaminodicyclohexyl methane, 1,4-diaminocyclohexane, 1,2-propylene diamine or even hydrazine, amino acid hydrazides, hydrazides of semi-carbazidocarboxylic acids, bis-hydrazides and bis-semi-carbazides.

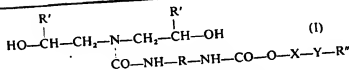
It may be particularly advantageous, especially in cases where relatively large quantities of hydrophilic groups are present, partly to offset the hydrophilicity with lateral hydrophobic groups. Suitable synthesis components are, for example, oleyl diethanolamine, stearyl diethanolamine, adducts of long-chain alkyl isocyanates with diethanolamine, esterification products of long-chain fatty acids with glycerol or trimethylol propane, adducts of C_{12} -amines or phenols with glycidol or 3-ethyl-3-hydroxymethyl oxetane.

In addition to the synthesis components which are difunctional in the isocyanate-polyaddition reaction it is also possible in certain cases, where branching of the polyurethanes is required, proportionately to use the synthesis components having a functionality of three or more which are known in polyurethane chemistry. This is particularly advantageous in cases where monofunctional hydrophilic polyethers are used. However, the average functionality of the synthesis components should preferably not exceed 2.1. Both ionic and also non-ionic compounds which are both monofunctional and also difunctional in the context of the isocyanate addition reaction may be used as hydrophilic synthesis components in the process according to the present invention. Such compounds include:

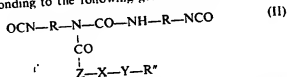
(a) diisocyanates having lateral hydrophilic chains containing ethylene oxide units and/or compounds which are difunctional in the isocyanate-polyaddition reaction containing isocyanate-reactive hydrogen atoms and having lateral hydrophilic chains containing ethylene oxide units and/or compounds which are hydrophilic chains containing ethylene oxide units and/or compounds which are monofunctional in the isocyanate-polyaddition reaction containing isocyanate-reactive hydrogen atoms and hydrophilic chains containing ethylene oxide units; and also

(b) any monoisocyanates or diisocyanates containing cationic groups or groups convertible thereto and/or compounds which are mono- or di-functional in the isocyanate-polyaddition reaction containing isocyanate-reactive hydrogen atoms and cationic groups or groups convertible thereto.

The preferred bifunctional hydrophilic synthesis components having lateral hydrophilic chains containing ethylene oxide units include both compounds corresponding to the following general formula:



and/or compounds corresponding to the following general formula:



Particularly preferred synthesis components (a) are those corresponding to general formula (I) above.

In general formulae (I) and (II) above, R represents a difunctional radical of the type obtained by removing the isocyanate groups from a diisocyanate corresponding to the general formula: $\text{R}(\text{NCO})_2$, of the above-mentioned type;

R' represents hydrogen or a monofunctional hydrocarbon radical containing from 1 to 8 carbon atoms, preferably a hydrogen atom or a methyl group;

R'' represents a monofunctional hydrocarbon radical having from 1 to 12 carbon atoms, preferably an unsubstituted alkyl radical having from 1 to 4 carbon atoms;

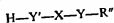
X represents a divalent radical obtained by removal of the terminal oxygen atom from a polyalkylene oxide chain having from 5 to 90, preferably from 20 to 70, chain members, of which at least 40%, preferably at least 65%, comprises ethylene oxide units and which, in addition to ethylene oxide units, may also comprise propylene oxide, butylene oxide or styrene oxide units, preferably propylene oxide units;

Y preferably represents oxygen or even $-\text{NR}'''$ — where in R''' corresponds in its definition to R''; and

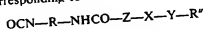
Z represents a radical which corresponds in its meaning to the definition of Y.

The compounds corresponding to general formulae (I) and (II) above may be produced by the methods according to German Offenlegungsschrift Nos. 2,314,512 and 2,314,513. In addition to the disclosures of these two Offenlegungsschriften, it is pointed out that, instead of using the monofunctional polyether alcohols mentioned therein as starting materials, it is also possible to use those of the type of the polyether segment of which, in addition to ethylene oxide units, also contains up to 60%, by weight, based on polyether segment, of propylene oxide, butylene oxide or styrene oxide units, preferably propylene oxide units. The presence of such "mixed polyether segments" may afford specific advantages in certain cases.

Other particularly preferred hydrophilic synthesis components for incorporating lateral or terminal hydrophilic chains containing ethylene oxide units are compounds corresponding to the following general formula:



and/or compounds corresponding to the following general formula:



wherein

X, Y, Z, R and R'' are as defined above; and

Y' corresponds in its meaning to Y, but may additionally represent $-\text{NH}-$. Monofunctional polyethers are preferably used, but only in molar quantities $\leq 10\%$, by weight, based on the polyisocyanate used, to guarantee the required high

molecular weight structure of the polyurethane elastomers. In cases where relatively large molar quantities of monofunctional compounds containing isocyanate are used, it is advantageous also to use trifunctional alkyne oxide polyethers are reactive hydrogen atoms, although the average functionality of the synthesis components (polyisocyanates and polyhydroxyl compounds) should preferably not exceed 2.1.

The monofunctional hydrophilic synthesis components may be produced in accordance with the processes described in German Offenlegungsschrift Nos.

2,314,512 and 2,314,513 and in United States Patent Nos. 3,905,929 and 3,920,598 by alkoxylating a monofunctional starter, such as *n*-butanol or *n*-methyl butylamine, using ethylene oxide and optionally another alkylene oxide, for example propylene oxide, and optionally further modifying (although this is less preferred) the monohydric polyether alcohols obtainable in this way by reaction with excess quantities of diisocyanates or by reaction with ammonia to form the corresponding primary aminopolyethers.

Synthesis components (b) essential to the present invention are preferably compounds which are mono- or di-functional in the isocyanate polyaddition reaction containing incorporated tertiary amine nitrogen atoms which, after the polyurethane has been synthesised, are converted into the corresponding ammonium ions by quaternisation and/or neutralisation. Examples of such compounds are mentioned in US Patent No. 3,479,310, column 4, lines 11 to 62. Suitable neutralising or quaternising agents are mentioned, for example, in the Patent in column 6, lines 14 to 25.

The compounds mentioned, for example, in US Patent No. 3,419,533, column 3, line 75 to column 4, line 51 may be used as synthesis components for the incorporation into the polyurethane of tertiary sulphonium groups which are less preferred than the ammonium groups.

Basically, it does not matter how the cationic centres are incorporated into the polyurethanes. For example, apart from the methods described in the two above-mentioned Patents, it is also possible to produce a polyurethane or NCO-terminated prepolymer containing epoxy groups and to introduce the basic centre by reacting the epoxy group with a primary or secondary amine, the thus-introduced basic centre subsequently being converted into the salt form by an inorganic or organic acid or an alkylating agent.

In the process according to the present invention, the type and quantity of the component (a) is selected in such a way that the polyurethanes according to the present invention contain from 2 to 10%, by weight, preferably from 4 to 8%, weight, of laterally or terminally incorporated ethylene oxide units, $-\text{CH}_2-\text{CH}_2-\text{O}-$, in the process according to the present invention, the type and quantity and degree of neutralisation or quaternisation of the components (b) is selected in such a way that the polyurethanes according to the present invention contain from 16 to 100 milliequivalents per 100 g, preferably from 16 to 40 milliequivalents per 100 g, of $=\text{N}^{\oplus}=$, and/or



The sum of the number of milliequivalents of incorporated ionic groups per 100 g of polyurethane and the number of "pseudomilliequivalents" of incorporated lateral ethylene oxide units per 100 g of polyurethane preferably amounts to from 20 to 120 and, with particular preference, to from 24 to 56.

One "pseudomilliequivalent" of laterally or terminally incorporated ethylene oxide units is to be understood to be the quantity of ethylene oxide units incorporated in a polyalkylene oxide chain which makes the same contribution towards the dispersibility of the polyurethane in water as one milliequivalent of incorporated ionic groups. (The effectiveness of the above-mentioned ionic groups in terms of the contribution thereof towards the dispersibility of the polyurethane is determined solely by the number of milliequivalents of ionic groups and not by the nature of the ionic groups). In the aqueous polyurethane dispersions, the average particle diameter of the dispersed polyurethane particles depends upon the concentration of the incorporated hydrophilic centres in the polyurethane. Thus, the average particle size generally increases with decreasing concentration of hydrophilic centres for otherwise the same structure of the polyurethane. Exhaustive studies conducted by us have shown that, with otherwise exactly the same molecular structure, the ionic groups in any water-dispersible, exclusively same molecular structure polyurethane may always be replaced by a certain quantity of ionically modified polyurethane arranged laterally in a polyether chain in such a way that a corresponding, exclusively non-ionically modified polyurethane is obtained which, when dispersed in water, has the same average particle size (assuming that the polyurethane dispersion has been produced by an analogous method) when the milliequivalents of ionic groups present in the ionically modified polyurethane are replaced by the same number of "pseudomilliequivalents" of non-ionic groups. Thus, 0.5 g of ethylene oxide units laterally incorporated in a polyether chain

correspond to one milliequivalent of incorporated ionic groups. Accordingly, one "pseudomilliequivalent" of non-ionic groups is equivalent to 0.5 g of ethylene oxide units incorporated laterally in a polyether chain. This means that, for example, an aqueous dispersion of an exclusively ionically-modified polyurethane containing 16 milliequivalents per 100 g of one of the above-mentioned ionic groups contains dispersed polyurethane particles having the same average particle diameter as an analogously synthesised and produced, exclusively non-ionically-modified polyurethane dispersion containing 8 g per 100 g of ethylene oxide incorporated in a polyether chain.

The process according to the present invention for producing the self-dispersible polyurethanes may be carried out in accordance with the methods known in polyurethane chemistry both by the one-stage process and also by the two-stage process (prepolymer process).

For producing the self-dispersible polyurethanes, the reactants are generally used in an equivalent ratio of isocyanate groups to isocyanate-reactive groups of from 0.8:1 to 2.5:1, preferably from 0.95:1 to 1.5:1. The use of an NCO excess naturally results in the formation of compounds containing NCO groups which, when converted into an aqueous dispersion, react further with the water, accompanied by chain-extension, to form the dispersed end product. Accordingly, the above equivalent ratio embodies all the components involved in the synthesis of the polyurethanes according to the present invention, including the amino-group-containing chain-extender optionally used in the form of aqueous solutions, but not the proportion of water used for dispersing the polyurethanes which reacts with any NCO-group-containing compounds present in a chain-extending reaction.

Both the one-stage process and the two-stage process may be carried out in the presence or absence of solvents. Suitable solvents, especially if, as described below, it is intended to convert the polyurethanes into an aqueous dispersion during or after the production thereof, are, for example, water miscible solvents that are inert with respect to isocyanate groups and which boil at temperatures below 100°C, such as acetone or methyl ethyl ketone.

For carrying out the one-stage process, generally the difunctional compounds containing terminal isocyanate-reactive groups and having molecular weights of from 500 to 6000 mentioned under (1) to (7) above are mixed with the hydrophilic components (a) and (b) and with the optional chain-extender having a molecular weight below 300. The diisocyanate component is then added to the thus-obtained mixture in the absence of solvents, after which the reaction mixture is reacted, preferably at temperatures of from 50 to 150°C, and optionally after the addition of catalysts known in polyurethane chemistry. The quantity in which the diisocyanate components are used is generally such that an NCO:OH ratio of from 0.8:1 to 1.05:1 prevails. During the reaction, the viscosity of the reaction mixture increases so that one of the above-mentioned solvents is gradually added to the mixture. Finally, an organic solution of the fully reacted polyurethane is obtained, its concentration preferably being adjusted to from 10 to 70%, by weight, more especially to from 15 to 55%, by weight, expressed as solids. In this one-stage process, it is particularly recommended to use tertiary amines containing two alcoholic hydroxylic groups as component (b). In cases where component (b), it is recommended to effect this cationic groups are used as component (b), it is recommended to effect this

conversion by known neutralisation or quaternisation after the polyurethane in the reaction either in organic solution or in such a way that the polyurethane in the form of an organic solution is neutralised during its conversion into an aqueous dispersion by neutralising agents present in the water.

In that case, the dissolved polyurethane elastomers are best converted into an aqueous dispersion by adding water to the stirred solution. In many cases, the solution passes through the phase of a water-in-oil emulsion, after which it changes into an oil-in-water emulsion, simultaneously overcoming a viscosity maximum.

Removal of the solvent by distillation leaves behind a pure aqueous stable dispersion.

For carrying out the two-stage process, an NCO-prepolymer is preferably initially prepared in the melt from excess diisocyanates, relatively high molecular weight compound having isocyanate-reactive groups of the type exemplified in (1) to (7) above and hydrophilic components (a) and (b), maintaining an NCO/OH ratio generally of from 1.1:1 to 3.5:1, preferably from 1.2:1 to 2.5:1, in the absence of solvents or even in the presence of solvents. Where it is prepared in the absence of solvents, the NCO-prepolymer is subsequently taken up, for example in a suitable solvent. The thus-obtained solution of the prepolymer may then be reacted

in known manner with the chain-extender having a molecular weight below 300 of the type exemplified above. To prepare the polyurethane dispersions according to the present invention, it is particularly recommended to adopt a particular embodiment of the two-stage process in which water or a water/solvent mixture is added in small quantities to the described solution of the NCO-prepolymer with the solution of the chain-extender (in this case the above-mentioned diamines and the hydrazine derivatives are preferably used as chain-extenders) in such a way that the NCO:OH-ratio is from 2.5:1 to 1.05:1. This reaction may be carried out at room temperature or, preferably, at temperatures of from 25 to 60°C. By subsequently adding the rest of the water and removing the solvent, the polyurethane dispersion is finally obtained. However, it is also possible in this embodiment of the process to dissolve the chain-extender in the total quantity of the water ultimately present in the dispersion (generally from 50 to 200%, by weight, based on solid polyurethane).

However, the two-stage process described above may also be carried out in the absence of solvents without any real difficulties by preparing the described NCO-prepolymer in solvent-free form and stirring it as a melt into the water. In this case, too, the above-mentioned chain-extenders containing amino groups may be used in solution in the water.

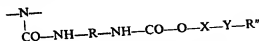
The water-dispersible polyurethane elastomers according to the present invention are of predominantly linear molecular structure and are characterized by a content of ethylene oxide laterally or terminally incorporated in a polyether chain of from 2 to 10%, by weight, preferably from 4 to 8%, by weight, and by a content of

=N= and/or

=S^{VI}

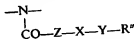
groups of from 16 to 100 milliequivalents, preferably from 16 to 40 milliequivalents per 100 g. The lateral polyalkylene oxide chain which contains the ethylene oxide units essential to the present invention is preferably attached through groups:

(i) corresponding to the following general formula:



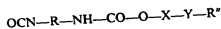
or

(ii) corresponding to the following general formula:



wherein R, R^{*}, R^{''}, X, Y and Z are as defined above.

The process according to the present invention as described above merely represents the preferred method, but by no means the only method of obtaining the polyurethanes according to the present invention. Another method of obtaining the polyurethanes according to the present invention is, for example, to introduce the nonionic lateral hydrophilic groups into a preferably linear polyurethane elastomer already containing ionic groups or groups convertible thereto by reacting this elastomer with hydrophilic monoisocyanates corresponding to the following general formula:



wherein

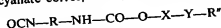
R, X, R^{*} and R^{''} are as defined above.

Hydrophilic monoisocyanates of this type are produced in analogy to the process described in German Offenlegungsschrift No. 2,314,512, although it is pointed out in addition to the disclosure of the Offenlegungsschrift that, instead of using the monofunctional polyether alcohols mentioned there as starting materials, it is also possible to use those of which the polyether segment, in addition to ethylene oxide units, also contains up to 60%, by weight, preferably up to 35%, by weight, based on polyether segment, of propylene oxide, butylene oxide or styrene oxide units, preferably polyethylene oxide units.

In cases where the polyurethanes according to the present invention are produced using these hydrophilic monoisocyanates, a linear polyurethane is preferably prepared from the above-mentioned starting materials using an

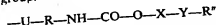
equivalent ratio of isocyanate groups to isocyanate-reactive groups of preferably 1:1, the thus-prepared linear polyurethane containing ionic groups or groups convertible thereto, but still no hydrophilic polyether segments. This linear polyurethane elastomer is then reacted in the melt or in a suitable solvent, for example of the type mentioned above, with the hydrophilic monoisocyanates generally at from 50 to 150°C, producing above all an addition of the isocyanate group of the hydrophilic monoisocyanate with the active hydrogen atoms of the urethane and/or urea groups present in the linear polyurethane. Any groups convertible into ionic groups which may present are then at least partly converted into the corresponding ionic groups by known neutralisation or quaternisation.

In another particularly preferred procedure, a prepolymer containing terminal NCO-groups is reacted with a monofunctional hydrophilic polyether so that a polymeric polyurethane having terminal hydrophilic polyether segments is formed. Such a product may, of course, also be obtained by a one-stage process by using a hydrophilic monofunctional polyether as synthesis component in the synthesis of the polyurethane. Furthermore, it is, of course, also possible to react a polymer containing terminal OH, SH, NH₂, NHR or COOH-groups with a hydrophilic monoisocyanate corresponding to the following general formula:



wherein

R, X, Y and R* are as defined above.
This group of polyurethanes according to the present invention is characterised by the group:



wherein

U represents $-\text{O}-\text{CO}-\text{NH}-$, $-\text{NH}-\text{CO}-\text{NH}-$, $-\text{NH}-\text{CO}-$ or $-\text{S}-\text{CO}-\text{NH}-$; and R, X, Y and R* are as defined above.

In cases where polyurethanes containing terminal monofunctional hydrophilic polyethers are produced, provision is preferably made for an at least weak branching of these products, for example by the proportionate use of trifunctional or higher polyfunctional synthesis components or by partial allophanate formation, the trimerisation or biuret formation, although the average functionality of the synthesis components preferably does not exceed 2.1.

The polyurethane according to the present invention thus obtained either in the form of a melt or in the form of a solution, may then be converted into an aqueous dispersion by mixing with water and distilling off the auxiliary solvent used, if any.

Basically, the polyurethanes according to the present invention may be converted into aqueous dispersions by any methods including, for example, dispersion in the absence of solvents, for example by mixing the polyurethane melt with water in apparatus which is able to generate high shear gradients and the use of very small quantities of solvent for plasticisation during processing in the same apparatus, also the use of non-mechanical dispersion aids, such as soundwaves of extremely high frequency. Furthermore, in the case of polyurethane ureas, too, chain-extension may be carried out after the prepolymer has been converted into an aqueous emulsion. However, it is also possible to use simple mixers, for example stirrer-equipped vessels or so-called "flow mixers", because the polyurethanes according to the present invention are self-dispersible.

The polyurethanes dispersed in accordance with the present invention generally have an average particle size of $\leq 300 \text{ m}\mu$, preferably from 50 to 300 mμ, more preferably from 10 to 250 mμ.

This is the particle size range in which conventional cationic dispersions show their greatest sensitivity to additions of electrolyte. The dispersions are opaque to translucent and show a pronounced Tyndall effect, especially when they are diluted to a solids content of about 10%, by weight.

The rheological behaviour of the dispersions, which it is not intended to discuss in detail here, is governed by the particle size and concentration. In the case of relatively small particles, viscosity increases, in addition to which an increasingly higher flow limit occurs below a particle size of about 100 mμ (Bingham substance). Irrespective of this dependence, viscosity increases with increasing concentration which, with this class of dispersions, may amount to as much as 65%, in some cases up to a level of 50P.

10

Despite the presence therein of cationic groups, the dispersions are largely unaffected by electrolytes. This provides, for example, for the acid-catalysed crosslinking of the latex particles with formaldehyde or formaldehyde derivatives; similarly, they may be pigmented using electrolyte-active pigments or dyes.

5

The dispersions may be blended with other cationic or non-ionic dispersions, such as polyvinyl acetate, polyethylene, polystyrene, polybutadiene, polyvinyl chloride, polyvinyl acrylate and copolymer plastics dispersions. The addition of known chemically non-fixed, preferably ionic, emulsifiers is also possible, but, of course, not essential.

10

Furthermore, fillers, plasticisers, pigments, carbon black and silica sols, aluminium, clay and asbestos dispersions may also be incorporated into the dispersions.

15

The dispersions of the polyurethane compositions in water are generally stable, storable and transportable and may be processed at any later stage, for example by forming. In general, they dry directly into dimensionally stable plastics coatings, although forming of the end products may also be carried out in the coatings, although forming of the end products may also be carried out in the presence of known cross-linking agents. Polyurethanes having different properties are obtained according to the chemical composition selected and to the urethane group content. Thus, it is possible to obtain soft, tacky compositions, thermoplastic and elastomeric products having a variety of different hardnesses up to glass-hard and duroplasts. The hydrophilicity of the products may also vary within certain limits. The elastic products may be thermoplastically processed at elevated temperatures. For example at from 100 to 180°C, providing they are not chemically cross-linked.

20

25

The end products of the process are suitable for coating and impregnating woven and non-woven textiles, leather, paper, wood, metals, ceramics, stone, concrete, bitumen, rigid fibres, straw, glass, porcelain, various types of plastics, glass fibres, for antistatic and crease-resistant finishing, as binders for non-wovens, adhesives, adhesion promoters, laminating agents, hydrophobising agents, plasticisers, bishen products, for example for cork powder or sawdust, glass fibres, asbestos, paper-like materials, plastics or rubber waste, ceramic materials, as auxiliaries in textile printing and in the paper industry, as additives to polymers, as sizing agents, for example for glass fibres, and for finishing leather.

30

35

The dispersions or pastes are preferably applied to a porous substrate which subsequently remains bonded to the end product, such as woven or non-woven textile structures and fibre mats, or non-wovens, also paper webs, foam sheet of split leather which, by virtue of the absorbing action thereof, cause the coating to harden immediately. This is followed by drying at elevated temperature and, optionally, pressing. However, drying may also be carried out on smooth porous or non-porous materials, for example metal, glass, paper, cardboard, ceramic materials, sheet steel, silicone rubber, aluminium foil, the resulting sheet-form structure subsequently being lifted off and used as such or applied to a substrate using a reversal process by bonding, flame lamination or calendaring. Application by a reversal process may be carried out at any time.

40

45

50

The properties of the end products may be modified by using vinyl polymers or active or inactive fillers. It is possible to use, for example, polyethylene, polypropylene, polyvinylacetate, ethylene-vinylacetate copolymers which may optionally be (partially) hydrolysed and/or grafted with vinyl chloride, styrene, butadiene copolymers, ethylene (graft) copolymers, polyacrylates, carbon black, silica, asbestos, talcum, kaolin, titanium dioxide, glass in the form of powder or in the form of fibres or cellulose. Depending upon the required property spectrum the application envisaged for the end products, up to 70%, based on total dry substance, of these fillers may be present in the end product.

55

60

Dyes, pigments, plasticisers or additives which influence the flow properties may, of course, also be added.

Drying of the products obtained by various application techniques may be carried out either at room temperature or at elevated temperature. The drying to be selected in each individual case, which is governed not only by temperature but also by the chemical composition of the material, but above all by moisture content, the drying time and the layer thickness, is readily determined by a preliminary test. For a given heating time, the dry temperature must always be below the solidification temperature.

The sheet structures may then be coated with a finish order to increase their surface resistivity. Aqueous dispersions or solutions are again preferably used for this purpose.

Extremely rigid polyurethanes obtained from finely divided dispersions and

65

65

sols are suitable for use as stoving lacquers and, in some cases, even as air-drying lacquers. They combine extreme hardness and elasticity with high gloss and, in cases where aliphatic diisocyanates are used, favourable light stability and weather resistance.

The following Examples illustrate the present invention.

EXAMPLE 1

- (a) Production of the non-ionic hydrophilic chain-extender:
The non-ionic hydrophilic chain-extender is produced in analogy to the process described in US Patent No. 3,905,929 by reacting equivalent parts of:

(i) a polyether monoalcohol of *n*-butanol, ethylene oxide and propylene oxide (in a molar ratio of 83:17) having an OH-number of 30,
(ii) 1,6-hexane diisocyanate and
(iii) diethanolamine.

The resulting diol has an average molecular weight of 2140.

- (b) Production of the cationic polyurethane (PU)-dispersion:
4970 parts, by weight, of a polyester diol of adipic acid, phthalic acid anhydride and ethylene glycol having an OH-number of 67, 16580 parts, by weight, of a polyester diol of phthalic acid anhydride and ethylene glycol having an OH-number of 56 and 1350 parts, by weight, of the above-described non-ionic hydrophilic chain-extender are dehydrated together for 30 minutes at 120°C in a vacuum of 15 Torr. After cooling to 80°C, 3377 parts, by weight, of 1,6-hexane diisocyanate are added all at once and stirred in for 10 minutes without heating. The mixture is stirred for 45 minutes at 80°C, with a total of 11060 parts, by weight, of followed by stirring for 1 hour at 60°C, 222 parts, by weight, of 1,2-diaminopropane is carefully diluted, beginning at 80°C, by weight, of N-methyl diethanolamine are added to the acetone solution stirred at 60°C and gently boiling under reflux. The solution is stirred for 1 hour at 60°C, 222 parts, by weight, of acetone and followed by rinsing with another 1580 parts, by weight, of acetone, after which, the solution is stirred for 1 hour at 60°C, 222 parts, by weight, of acetone and followed by rinsing with another 1580 parts, by weight, of acetone. The acetone solution is added, the solution is rinsed with another 1580 parts, by weight, of acetone and followed by a further 7110 parts, by weight, of acetone. The acetone solution is diluted with a further 7110 parts, by weight, of acetone. The acetone solution is then stirred at 60°C. 30 minutes after the amine has been added, 100 parts, by weight, of water and 1 part, by weight, of dibutyl tin dilaurate are added, followed by dilution with 10270 parts, by weight, of acetone.

After 6 hours, no more isocyanate may be detected in the acetone solution by IR-spectroscopy. 500 parts, by weight, of dimethyl sulphate dissolved in 1580 parts, by weight, of acetone are added, the solution is stirred for 1 hour at 50°C and 36000 parts, by weight, of water preheated to 50°C are allowed to run in slowly over a period of 30 minutes, again at 50°C.

After the acetone has been distilled off in a water pump vacuum at 50°C, 1500 parts, by weight, of a 30% aqueous formaldehyde solution are added, giving 60,000 parts, by weight, of a stable cationic polyurethane dispersion which, for a solids content of 43%, by weight, has a pH value of 4.2 and a particle size (diameter determined by the diffusion of light) of from 142 to 149 nm.

Electrolyte stability:

50 g of a sample of this dispersion adjusted to a solids content of 10%, by weight, require 80 ml of a 10%, by weight, NaCl-solution for coagulation at room temperature. A corresponding PU-dispersion produced without the non-ionic hydrophilic emulsifier coagulates after the addition of only 3.4 ml of NaCl-solution under the same test conditions.

- (c) General procedure for determining the electrolyte stability of cationic PU-dispersions:

50 ml of a cationic PU-dispersion, adjusted to a solids content of 10%, by weight, are introduced into an Erlenmeyer flask, followed by the dropwise addition with vigorous stirring (magnetic stirrer) at room temperature of 10%, by weight, aqueous NaCl solution from a burette. After increasing thickening, the dispersion undergoes generally sudden coagulation, in any case with a consumption of sodium chloride solution of <20 ml. With even higher electrolyte stability, difficulties are occasionally involved in determining the end point because coagulation takes place slowly with partial flocculation. In this case, end point determination is facilitated by adding the sodium chloride solution in 5 ml portions, stirring for 5 minutes after each addition and then making the assessment.

12

EXAMPLE 2

The dependence of electrolyte stability upon the quantity of ethylene oxide units used is illustrated by this Example.

(a) 86.3 parts, by weight, of a polyester diol of adipic acid, phthalic anhydride and ethylene glycol having an OH-number of 67, 307.7 parts, by weight, of a polyester diol of phthalic acid anhydride and ethylene glycol having an OH-number of 56 and 17.2 parts, by weight, of a polyether monoalcohol of *n*-butanol, ethylene oxide and propylene oxide (molar ratio 83:17) having an OH-number of 26 are combined and dehydrated for 30 minutes at 120°C/15 Torr. After cooling to 80°C, 67.2 parts, by weight, of 1,6-hexane diisocyanate are added and mixed in without heating over a period of 10 minutes, followed by stirring for another 110 minutes at 120°C. The NCO-content is determined (3.12% by weight) and, after cooling to 60°C, the mixture is diluted with 80 parts, by weight, of acetone. 11.9 parts, by weight, of *N*-methyl diethanolamine are added, followed by stirring for 1 hour at 60°C, after which the mixture is diluted with another 80 parts, by weight, of acetone, 6.6 parts, by weight, of 1-aminomethyl-5-amino-1,3,3-trimethyl cyclohexane and 1.94 parts, by weight, of hydrazine monohydrate are successively added, the mixture is stirred for 30 minutes at 60°C, diluted with another 160 parts, by weight, of acetone, quaternised for 1 hour with 8.4 parts, by weight, of chloroacetamide, 11 parts, by weight, of 85% *o*-phosphoric acid are added and, finally, 1125 parts, by weight, of water are run in, resulting in the formation of a finely divided, bluish translucent dispersion which, after the acetone has been distilled off *in vacuo* (15 Torr, bath temperature 50°C), has a solids content of 30% by weight, a pH value of 4.2 and an average particle diameter of from 143 to 147 nm. The dispersion is extremely temperature-stable, withstanding tempering at 85°C for 24 hours without any change in its particle size.

For a content of 2.6% by weight, of ethylene oxide units, based on PU-solids, 50 ml of a sample of this dispersion, adjusted to a solids content of 10%, by weight, consume 5 ml of 10% by weight, aqueous sodium chloride solution before coagulation.

(b) A dispersion is prepared in the same way as in Example 2(a), except that the quantity of hydrophilic polyether is increased to 21.5 parts, by weight, and, hence, the content of ethylene oxide units, based on PU-solids, to 3.3% by weight. As a result electrolyte stability is increased. 50 ml of a sample 2(b) adjusted to a solids content of 10%, by weight consume 17.5 ml of a 10% by weight, sodium chloride solution before coagulation.

(c) A dispersion is prepared in the same way as in Example 2(b), except that the quantity of hydrophilic polyether is increased to 25.8 parts, by weight, and, hence, the content of ethylene oxide units, based on PU-solids, to 3.9% by weight. As a result, electrolyte stability is increased. 50 ml of a sample 2(c) adjusted to a solids content of 10% by weight, consume 30 ml of a 10% by weight, sodium chloride solution before coagulation.

(d) A dispersion is prepared in the same way as in Example 2(c) except that the quantity of hydrophilic polyether is increased to 30 parts, by weight, corresponding to 4.5% by weight, of ethylene oxide units, based on PU-solids. As a result, electrolyte stability is increased. 50 ml of a sample 2(d) adjusted to a solids content of 10% by weight, consume 70 ml of a 10% by weight, sodium chloride solution before coagulation.

EXAMPLE 3

The dependence of electrolyte stability upon particle size is illustrated in this Example using dispersions of the same composition.

Polyurethane dispersions are prepared from the following starting materials by the method described in Example 2:

65 parts, by weight, of a polyester diol of adipic acid, phthalic acid anhydride and ethylene glycol, OH-number 67
 222.6 parts, by weight, of a polyester diol of phthalic acid anhydride and ethylene glycol, OH-number 56
 16.7 parts, by weight, of non-ionic hydrophilic chain-extender according to Example 1
 50 parts, by weight, of 1,6-hexane diisocyanate
 8.8 parts, by weight, of methyl diethanolamine
 5.7 parts, by weight, of 1-aminomethyl-5-amino-1,3,3-trimethyl cyclohexane
 1.6 parts, by weight, of hydrazine monohydrate

6.2 parts, by weight, of chloroacetamide
8 parts, by weight, of *o*-phosphoric acid (85%)
844 parts, by weight, of water.

By varying the production conditions (e.g. time and temperature variation during prepolymer formation and quantity of solvent), dispersions having the same chemical composition, but differing in particle size, were obtained. The electrolyte stability of these dispersions was determined by the method described in Example 1. The results are set out in the following Table.

	Dispersion	Particle size ⁽¹⁾ (nm)	Electrolyte stability ⁽²⁾
	A	81—83	2
	B	91—94	6
	C	101—102	6.5
	D	119—123	8
	E	140—143	11
	F	159—165	12
	G	232 ⁽³⁾	80
	H	300 ⁽³⁾	130

⁽¹⁾ average particle diameter, as determined by light dispersion

⁽²⁾ quantity in ml of 10%, by weight sodium chloride solution which is required to coagulate 50 ml of the dispersion, adjusted to a solids content of 10%, by

⁽³⁾ irregular, fairly wide dispersion.

EXAMPLE 4

340 parts, by weight, of a polyester diol of 1,6-hexane diol, 2,2-dimethyl-1,3-propane diol and adipic acid having an OH-number of 65 and 21.5 parts, by weight, of a polyether monoolcohol having an OH-number of 26 (according to Example 2) are dehydrated for 30 minutes at 120°C/15 Torr. After cooling to 80°C, 67.2 parts, by weight, of 1,6-hexane diisocyanate are added, the mixture is stirred for 30 minutes at 80°C and then for 90 minutes at 120°C and the NCO-content of the prepolymer is then determined (3.53%, by weight, of NCO). After cooling, the solution is slowly diluted with 80 parts, by weight, of acetone beginning at 80°C. 9.5 parts, by weight, of *N*-methyl diethanolamine are added to the homogeneous solution (external temperature 70°C) which is then stirred for 1 hour and diluted with another 160 parts, by weight, of acetone. 8.5 parts, by weight, of 1-aminomethyl-5-amino-1,3,3-trimethyl cyclohexane and 2.5 parts, by weight, of hydrazine monohydrate are then successively added, after which the solution is stirred for 1 hour at an external temperature of 70°C and diluted with another 160 parts, by weight, of acetone, after which 6.7 parts, by weight, of chloroacetamide are added. When the IR-spectrum of a sample no longer shows an NCO-band, 11 g are added. 1100 parts, by weight, of water preheated to 50°C are run in and the acetone is distilled off in a water pump vacuum from the cationic PU-dispersion formed, the bath temperature being maintained at 50°C. The resulting stable dispersion has an average particle diameter of from 126 to 130 nm and a pH value of 4.2 for a solids content of 31%, by weight. Based on solids, the product contains 3.7%, by weight, of polyethylene oxide segments and 17 milliequivalents of quaternary nitrogen/100 g of polyurethane.

50 ml of a sample of this dispersion, adjusted to a solids content of 10%, by weight, require 110 ml of a 10%, by weight, NaCl solution for coagulation (electrolyte stability determined in accordance with Example 1).

WHAT WE CLAIM IS:—

1. An electrolyte-stable, water-dispersible elastomeric polyurethane cationomer having one or more lateral or terminal polyalkylene oxide polyether chains containing from 2 to 10% by weight based on the polyurethane, of ethylene oxide units and a content of



groups of from 16 to 100 milliequivalents per 100 g of polyurethane.

15

7. A process as claimed in claim 4 substantially as herein described.
8. A process as claimed in claim 4 substantially as herein described with reference to any one of the Examples.
9. A polyurethane when prepared by a process as claimed in any of claims 4 to 5
8.
10. An aqueous dispersion of a polyurethane as claimed in any of claims 1 to 3 or 9.
11. A dispersion as claimed in claim 10 having a solids content of from 10 to 10
45% by weight.
12. A dispersion as claimed in claim 10 or claim 11 having an average particle size of from 50 to 300 mμ.
13. A dispersion as claimed in claim 10 substantially as herein described.
14. A dispersion as claimed in claim 10 substantially as herein described with reference to any one of the Examples.

ELKINGTON & FIFE,
Chartered Patent Agents,
High Holborn House,
52/54 High Holborn,
London WC1V 6SH.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1980
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.